



# PROGRESS IN UNDERSTANDING EUV RESIST RELATED OUTGASSING AND CONTAMINATION

I. POLLENTIER, R. LOKASANI, AND R. GRONHEID



# OUTLINE

Imec infrastructure and qualification results

Simple Residual Gas Analysis (RGA) approach to quantify cleanable and non-cleanable contamination

Correlation of simple RGA approach to NXE witness sample (WS) results

Summary

# OUTLINE

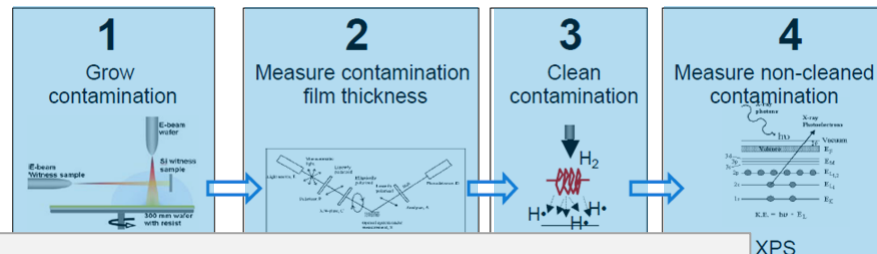
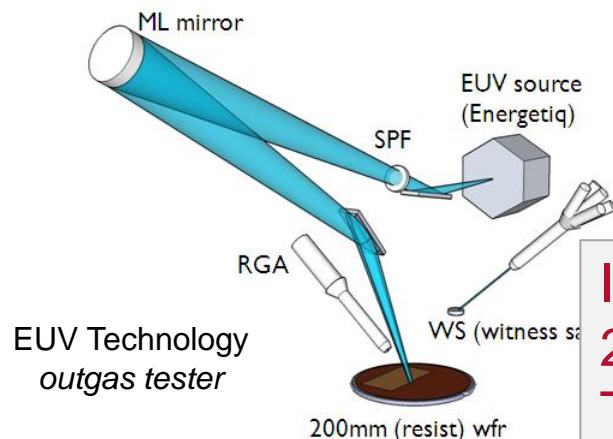
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# RESIST OUTGASSING QUALIFICATION PROCEDURE FOR NXE3x00



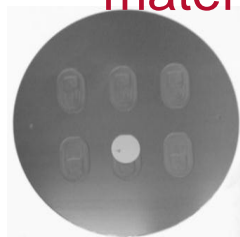
Imec infrastructure was certified end May 2012.

The issue with H-cleaner sulfur background is solved in August.

Currently, the infrastructure allows to test ~20 materials per month.



KLA-tencor UV1280 *ellipsometer*



200mm Pocket-wafer with 6 available positions for 1" WS



EUV Technology H-cleaner

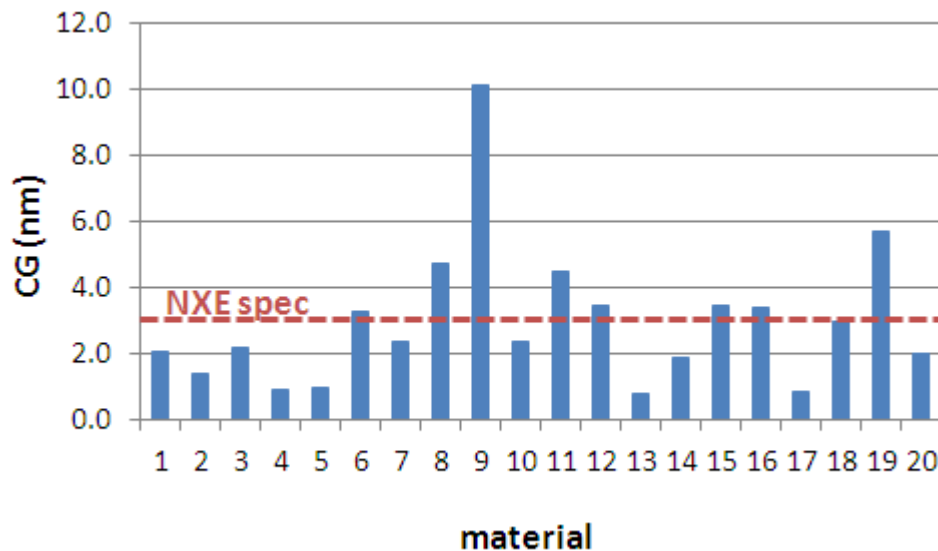


Thermo Instruments Theta 300 XPS

# CURRENT QUALIFICATION RESULTS

## Cleanable contamination

- ▶ Resist related contamination growth (CG) of 20 resists (commercial and model) was determined using NXE qualification method.

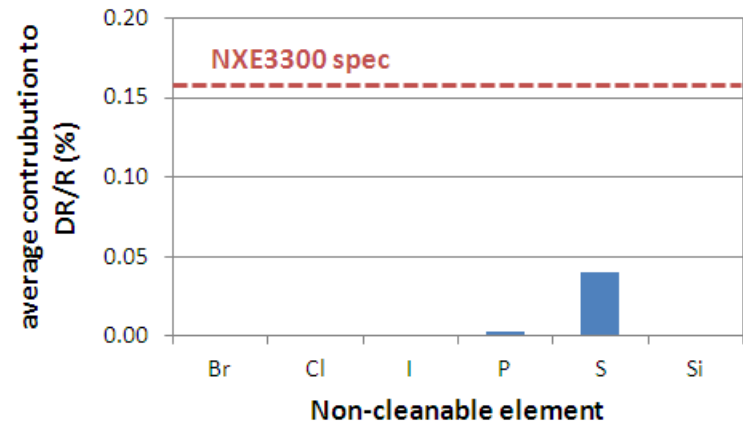
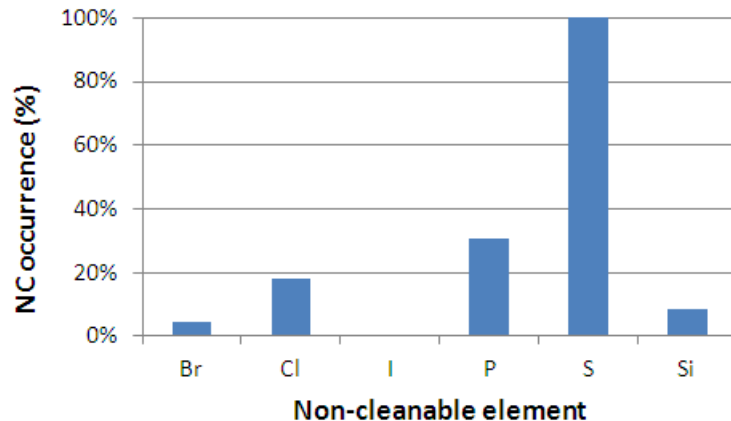


Most commercial materials meet the NXE spec for cleanable contamination (<3nm), but variation of CG thickness can be obtained depending on the chemistry of the (model) resists and its dose.

# CURRENT QUALIFICATION RESULTS

## Non-cleanable contamination

- ▶ Resist related contamination of 23 resists (commercial and model) was analyzed by XPS



Sulphur appears consistently in all measurements and has in average the highest contribution. However the typical contribution seems to be significantly less than the NXE300-spec.

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Imec infrastructure and qualification results

**Simple RGA approach to quantify cleanable and non-cleanable contamination**

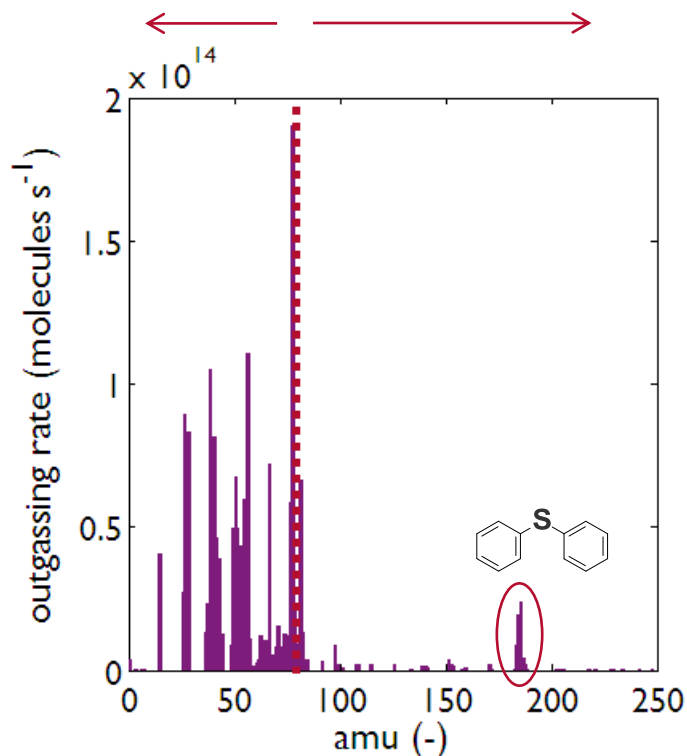
Correlation of simple RGA approach to NXE WS results

Summary

# RGa APPROACH FOR TESTING CONTAMINATION

WS testing is very relevant for contamination but gives limited information on the mechanism of outgassing and its relation to contamination

Non-contaminating outgassing      Contaminating outgassing



RGA can give continuously information on molecular weight (amu) of species that are outgassing.

Earlier work suggests that mostly high amu species contribute to contamination, while low-amu species do not.

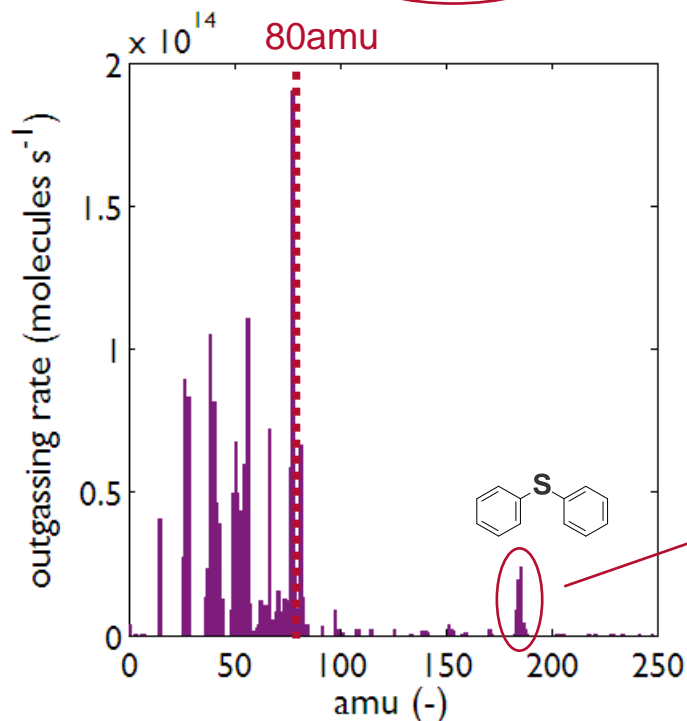
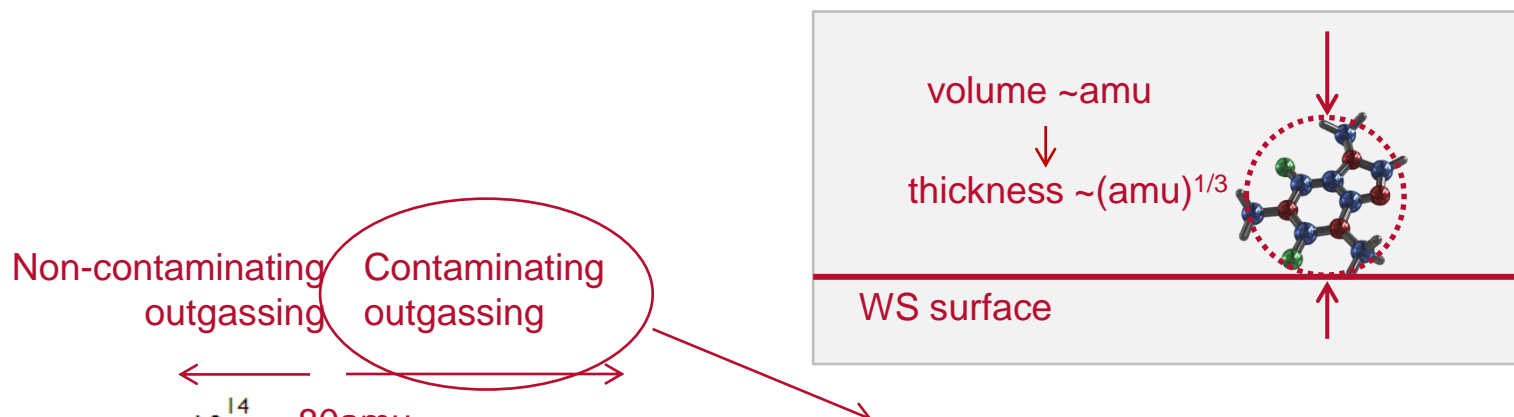
[I. Pollentier et al., Proc. of SPIE vol. 7972 (2011) ]

Non-cleanable contamination is typically seen as diphenylsulfide (or comparable) from PAG cation

[I. Pollentier et al., J. Photopolymer Sc. and Techn., Vol 23 (5) (2010)]



# SIMPLE RGA APPROACH TO QUANTIFY THE CONTAMINATION RELATED OUTGASSING



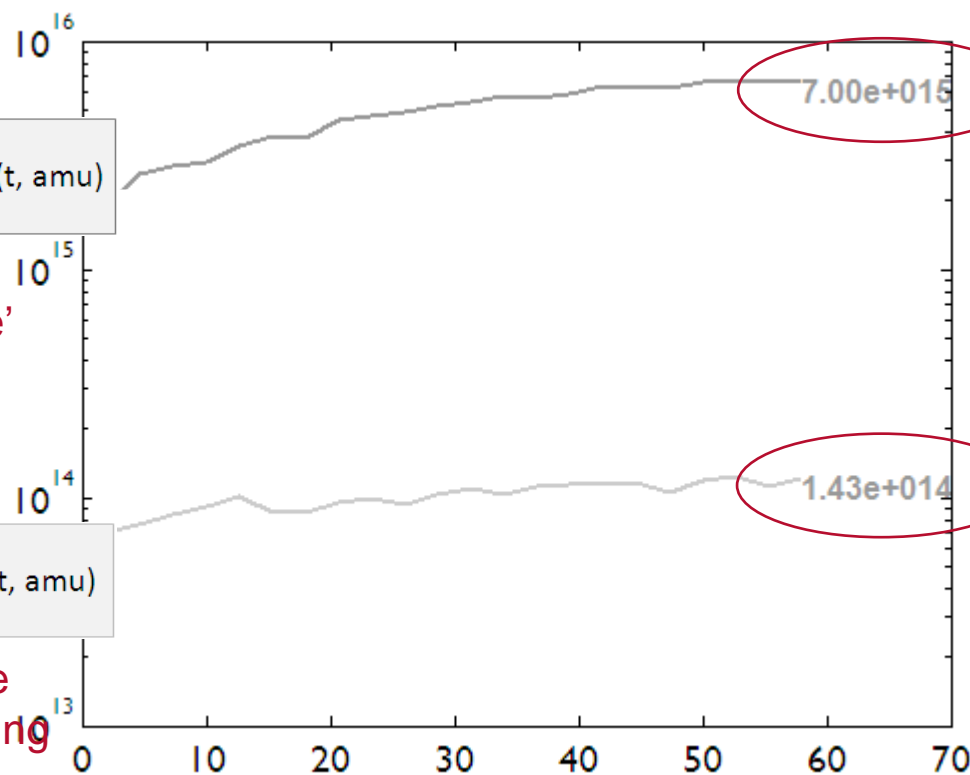
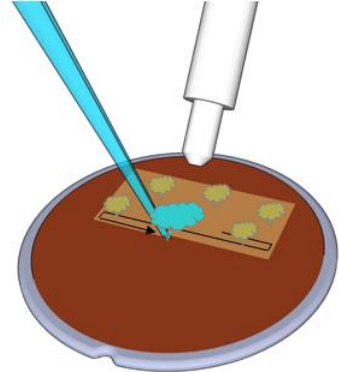
Total cleanable CG rate might be proportional to this outgassing rate :

$$\sum_{amu=80}^{250} (amu)^{1/3} \cdot \text{outgas}(t, amu)$$

Non-cleanable sulfur contamination rate might be related to this outgassing rate :

$$\sum_{amu=183}^{187} (amu)^{1/3} \cdot \text{outgas}(t, amu)$$

# SIMPLE RGA APPROACH TO QUANTIFY THE CONTAMINATION RELATED OUTGASSING



$$\sum_{amu=80}^{250} (amu)^{1/3} \cdot \text{outgas}(t, amu)$$

'cleanable CG outgassing rate'

$$\int_{t=0}^{1 \text{ hr}} \sum_{amu=80}^{250} (amu)^{1/3} \cdot \text{outgas}(t, amu) \cdot dt$$

'cleanable CG outgassing'

$$\sum_{amu=183}^{187} (amu)^{1/3} \cdot \text{outgas}(t, amu)$$

'non-cleanable sulphur outgassing rate'

$$\int_{t=0}^{1 \text{ hr}} \sum_{amu=183}^{187} (amu)^{1/3} \cdot \text{outgas}(t, amu) \cdot dt$$

'non-cleanable sulphur outgassing'

Integration of this outgassing rate is done over the time of evaluation (1hr); Outgassing rate is increasing due to the 'post-exposure' outgassing.

**Complex RGA information can be condensed in 2 parameters. Do they correlate with NXE qualification results?**

# OUTLINE

Imec infrastructure and qualification results

Simple RGA approach to quantify cleanable and non-cleanable contamination

**Correlation of RGA approach to NXE WS results**

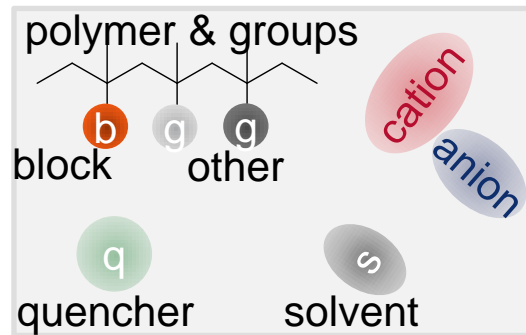
- ▶ Large resist family
- ▶ Changes in NXE qualification procedure

Summary

# CORRELATION OF RGA AND NXE FOR A LARGE RESIST FAMILY

In collaboration with JSR a DOE was done with 12 model resist with major chemical changes :

Different PAG chemistry and mixtures of PAGs  
Different protection groups (low and high activation energy) and mixing the groups in different ratios



Changes are much more than in earlier family definition.

I. Pollentier et al., Proc. of SPIE vol. 7972 (2011)

# CORRELATION OF RGA AND NXE FOR A LARGE RESIST FAMILY

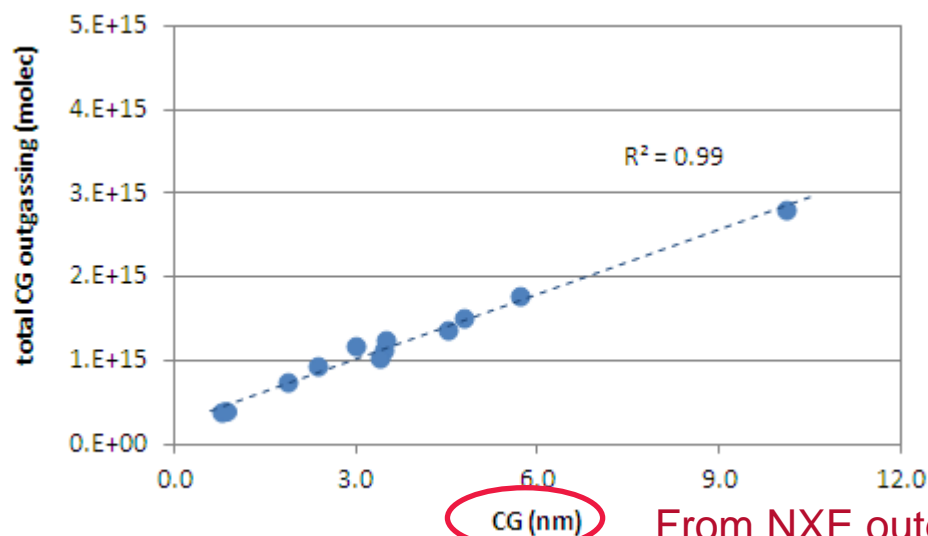
Different PAG chemistry and mixtures of PAGs  
Different protection groups (low and high activation energy) and mixing the groups in different ratios

Very good correlation is found !!!

Preliminary further tests show that model even works for adding UL or TC's on these materials !!!

'RGA cleanable CG  
outgassing'

$$\int_{t=0}^{1 \text{ hr}} \sum_{amu=80}^{250} (amu)^{1/3} \cdot \text{outgas}(t, amu) \cdot dt$$



From NXE outgassing  
WS test !

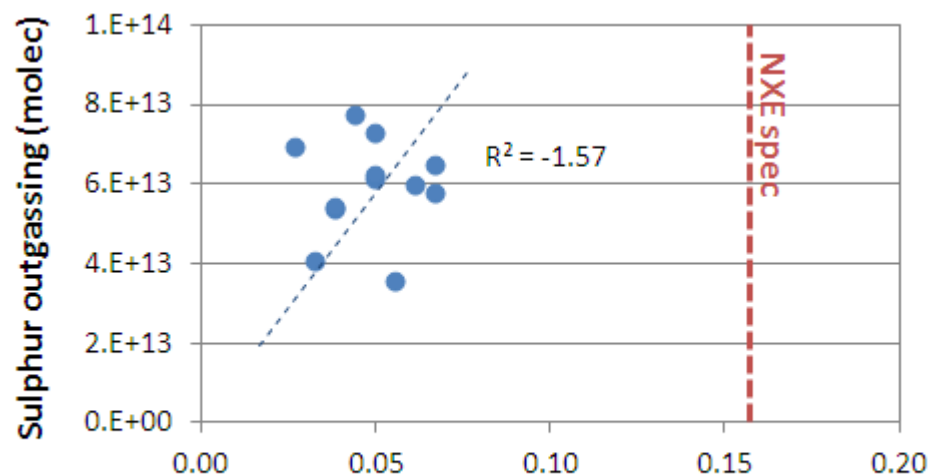
# CORRELATION OF RGA AND NXE FOR A LARGE RESIST FAMILY

Different PAG chemistry and mixtures of PAGs  
Different protection groups (low and high activation energy) and mixing the groups in different ratios

Poor correlation (possibly due to the very long H-cleaning time for some samples), but all well below the NXE-spec.

non-cleanable sulphur outgassing

$$\int_{t=0}^{1 \text{ hr}} \sum_{\text{amu} = 183}^{187} (\text{amu})^{1/3} \cdot \text{outgas}(t, \text{amu}) \cdot dt$$



XPS based Sulphur DR/R (%) From NXE outgassing WS test !

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Simple RGA approach to quantify cleanable and non-cleanable contamination

**Correlation of RGA approach to NXE WS results**

- ▶ Large resist family
- ▶ Changes in NXE qualification procedure

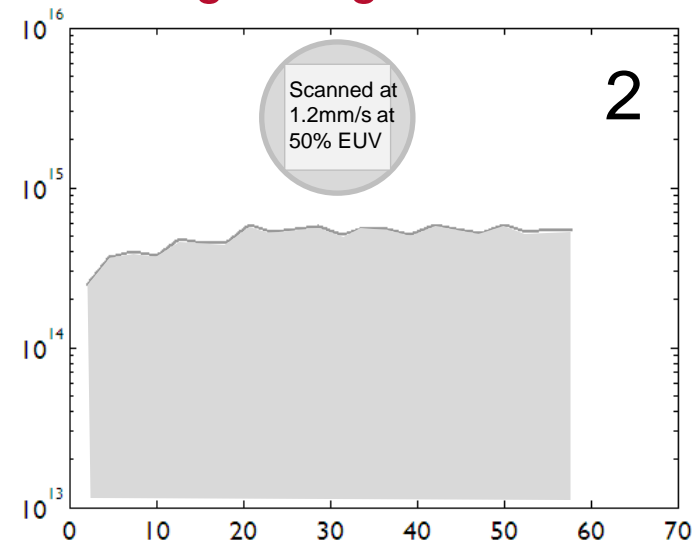
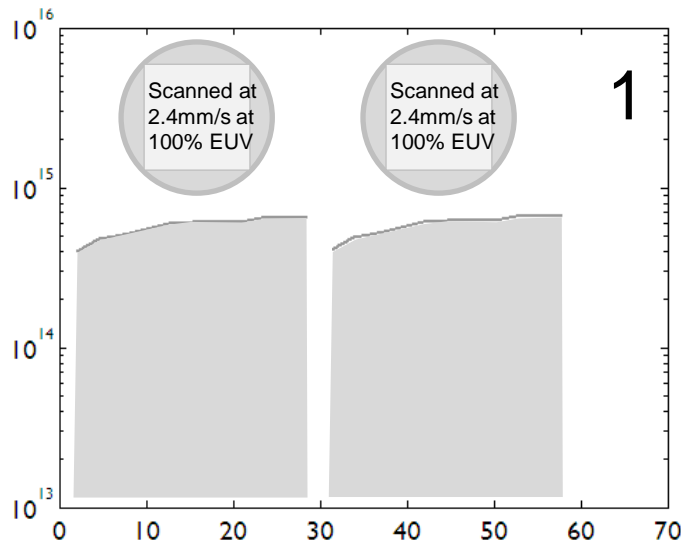
Summary

# CHANGES IN NXE PROCEDURE

Test	Scan speed (mm/s)	EUV intensity (a.u.)	Time (min)	Wfr area (cm <sup>2</sup> )	CG (nm)
<b>1</b>	<b>2.4</b>	<b>100%</b>	<b>2x30</b>	<b>2x200</b>	<b>2.15</b>
1b	2.4	100%	30	200	1.07
<b>2</b>	<b>1.2</b>	<b>50%</b>	<b>60</b>	<b>200</b>	<b>1.83</b>
2b	1.2	50%	45	150	1.27
2c	1.2	50%	30	100	0.65

Test to check if the '2-wfr' exposure could be replaced by a '1-wfr' for high-dose resists (all tests are done with std resist)

CG Differences suggest to be in line with integrated outgassing





# CHANGES IN NXE PROCEDURE

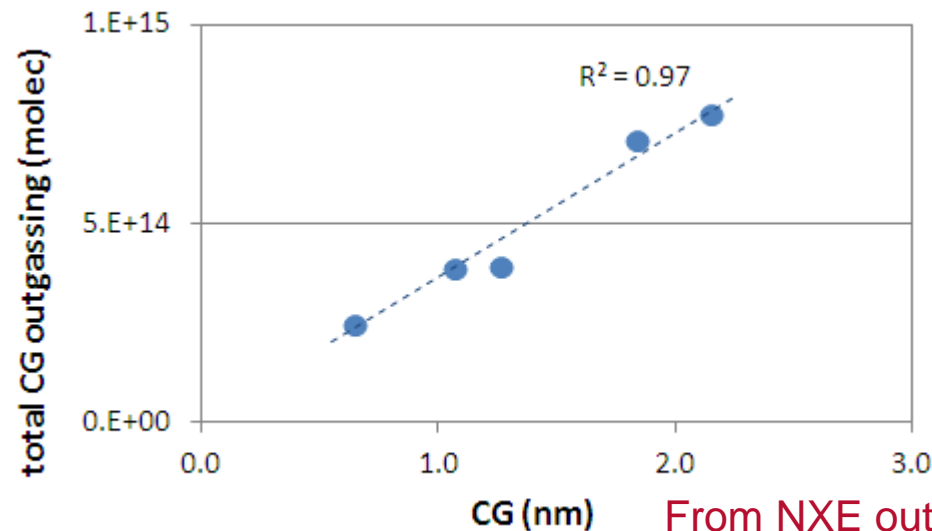
Test	Scan speed (mm/s)	EUV intensity (a.u.)	Time (min)	Wfr area (cm <sup>2</sup> )	CG (nm)
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Test to check if the '2-wfr' exposure could be replaced by a '1-wfr' for high-dose resists (all tests are done with std resist)

Good correlation between RGA and cleanable CG !

cleanable CG outgassing

$$\int_{t=0}^{x \text{ hr}} \sum_{amu=80}^{250} (amu)^{1/3} \cdot \text{outgas}(t, amu) \cdot dt$$



From NXE outgas procedure !

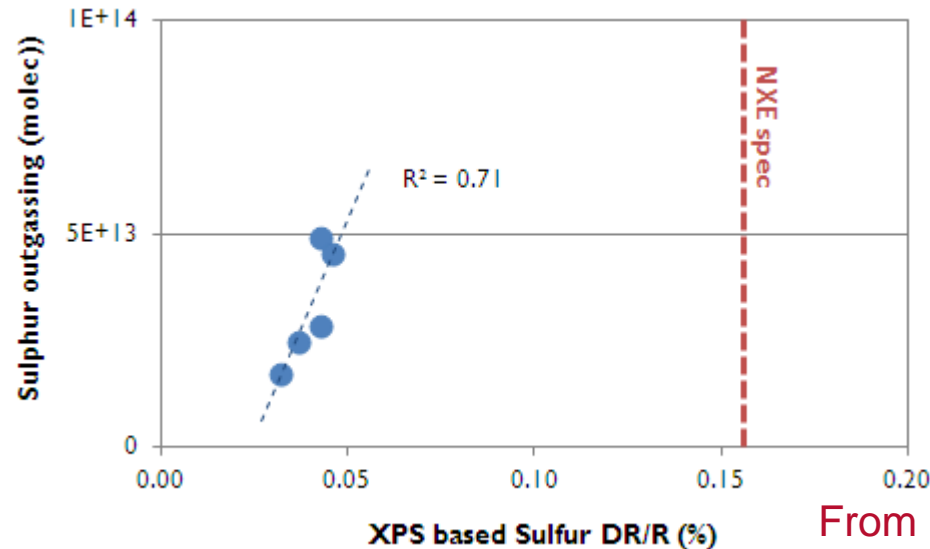
# CHANGES IN NXE PROCEDURE

Test to check if the '2-wfr' exposure could be replaced by a '1-wfr' for high-dose resists (all tests are done with std resist)

Less good correlation but possibly a trend is

non-cleanable sulphur outgassing

$$\int_{t=0}^{x \text{ hr}} \sum_{amu=183}^{187} (amu)^{1/3} \cdot \text{outgas}(t, amu) \cdot dt$$



From NXE outgas procedure !

# COMPARING THE 2 TEST CASES...

## supplier A

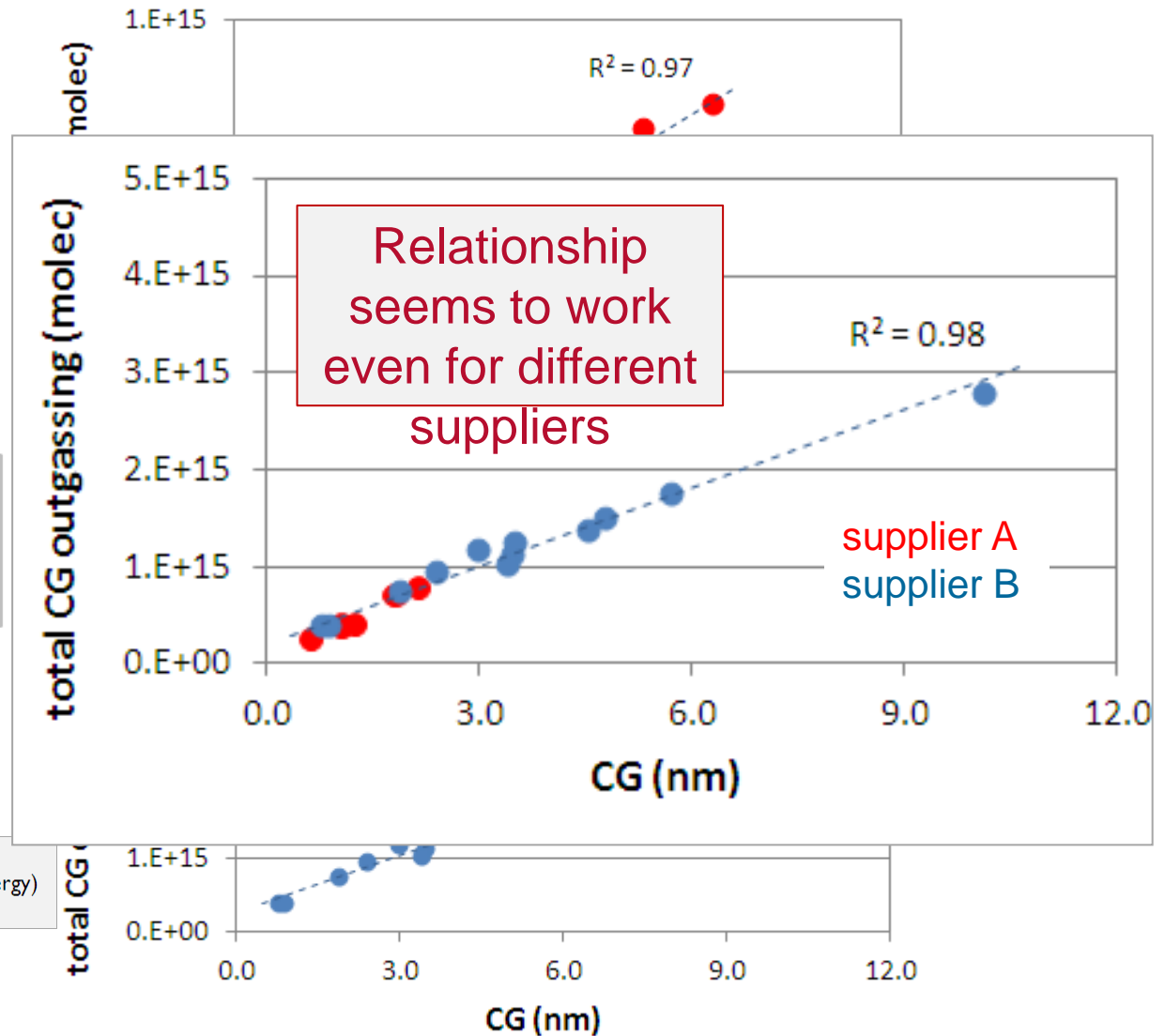
Test	Scan speed (mm/s)	EUV intensity (a.u.)	Time (min)	Wfir area (cm2)	CG (nm)
1	2.4	100%	2x30	2x200	2.15
1b	2.4	100%	30	200	1.07
2	1.2	50%	60	200	1.83
2b	1.2	50%	45	150	1.27
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'RGA cleanable CG outgassing'

$$\int_{t=0}^{1 \text{ hr}} \sum_{\text{amu} = 80}^{250} (\text{amu})^{1/3} \cdot \text{outgas}(t, \text{amu}) \cdot dt$$

## supplier B

Different PAG chemistry and mixtures of PAGs  
Different protection groups (low and high activation energy)  
and mixing the groups in different ratios



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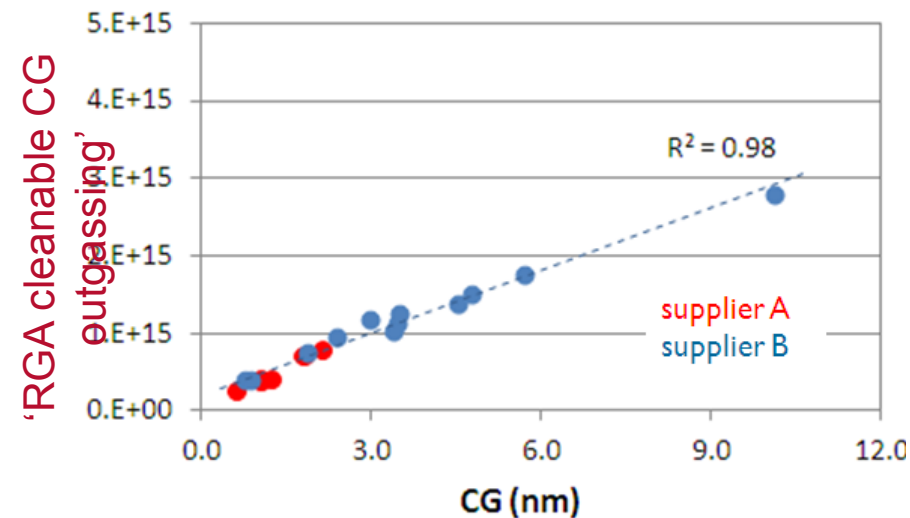
In the early experience of NXE resist outgas qualification cleanable contamination (chemistry, dose) seems more critical than non-cleanable contamination (mainly sulphur).

'RGA cleanable CG  
outgassing'

$$\int_{t=0}^{1\text{hr}} \sum_{amu=80}^{250} (amu)^{1/3} \cdot \text{outgas}(t, amu) \cdot dt$$

A semi-empirical simple RGA method is proposed based on weighted and integrated contribution of outgassing for cleanable and non-cleanable contamination.

For cleanable contamination, the RGA method seems to give excellent correlation with witness sample testing amongst different chemistries and suppliers. This suggests that this method can provide additional understanding and act as an alternative for faster qualification of materials.



# ACKNOWLEDGEMENTS

T. Conard (imec) for XPS support and helpful discussions

R. Perera and D. Houser (EUV Technology) for tool support

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